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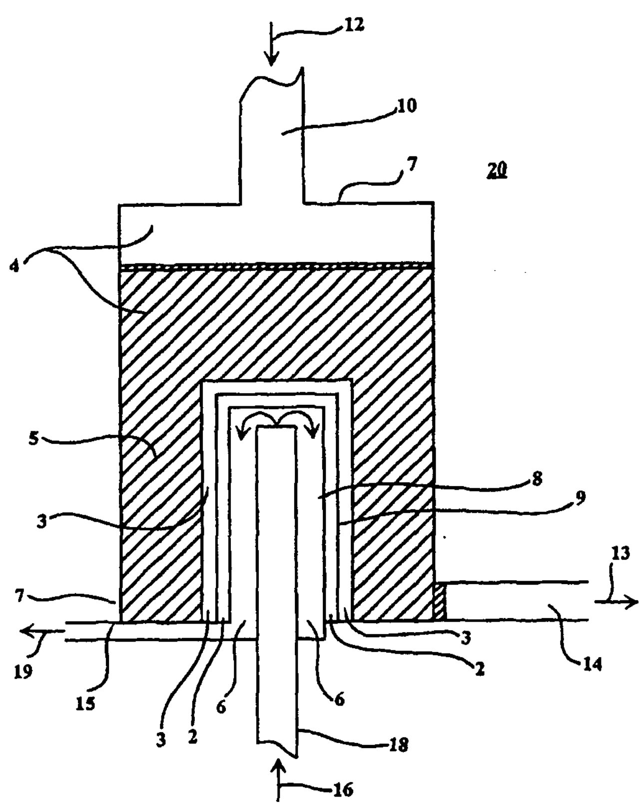
(54) Title: CATALYTIC MEMBRANE REACTOR WITH TWO COMPONENT THREE-DIMENSIONAL CATALYSIS

(57) Abstract

This invention relates to catalytic reactor membranes having a gas-impermeable membrane (2) for transport of oxygen anions. The membrane (2) has an oxidation surface and a reduction surface. The membrane (2) is coated on its oxidation surface with an adherent catalyst layer and is optionally coated on its reduction surface with a catalyst that promotes reduction of an oxygen-containing species (e.g., O_2, NO_2, SO_2, etc.) to generate oxygen anions on the membrane. The reactor (20) has an oxidation zone (4) and a reduction zone (6) separated by the membrane (2). A component of an oxygen-containing gas in the reduction zone (6) is reduced at the membrane (2) and a reduced species in a reactant gas in the oxidation zone (4) of the reactor is oxidized. The reactor (20) optionally contains a three-dimensional catalyst (5) in the oxidation zone (4). The adherent catalyst layer and the three-dimensional catalyst (5) are selected to promote a desired oxidation reaction, particularly a partial oxidation of a hydrocarbon. Preferred membrane materials of this invention are mixed metal oxides which are derived from brownmillerite and can, themselves, have brownmillerite structure. In a preferred embodiment, the oxygen reduction catalyst is Pd (5 wt. %) on $La_{0.8}Sr_{0.2}CoO_{3-x}$. The adherent catalyst layer is Ni (20 wt. %) on $La_{0.8}Sr_{0.2}MnO_3$ and the three-dimensional catalyst is Ni (5 wt. %) on alumina.



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CATALYTIC MEMBRANE REACTOR WITH TWO COMPONENT-THREE DIMENSIONAL CATALYSIS

FIELD OF THE INVENTION

This invention generally relates to catalytic partial and full oxidation of hydrocarbons and related reduced species using catalytic membrane reactors. Reactors containing gas-impermeable, solid state membranes with an adherent catalyst layer in combination with fixed (or packed)-bed catalyst are disclosed. Membrane materials, catalyst layers and packed-bed catalysts are selected to achieve a desired selective oxidation reaction. Catalytic membrane reactions include, among others, the partial oxidation of methane or natural gas to synthesis gas. The invention also relates to methods of using the catalytic membrane reactors to oxidize reactant gas and reduce oxygen-containing gas.

BACKGROUND OF THE INVENTION

Catalytic membrane reactors using solid state membranes for the oxidation or decomposition of various chemical species have been studied and used previously. One potentially valuable use of such reactors is in the production of synthesis gas. See, for example, Cable et al. EP patent application 90305684.4 (published November 28, 1990) and Mazanec et al. U.S. patent 5,306,411. Synthesis gas, a mixture of CO and H_2, is widely used as a feedstock in the chemical industry for production of bulk chemicals such as methanol and liquid fuel oxygenates. For most efficient use in the synthesis of methanol, the ratio of H_2:CO in synthesis gas should be adjusted to 2:1.

In a catalytic membrane reactor that facilitates oxidation/reduction reactions, a catalytic membrane separates an oxygen-containing gas from a reactant gas which is to be oxidized. Oxygen (O_2) or other oxygen-containing species (for example, NO_x or SO_x) are reduced at one face of the membrane to oxygen anions that are then transported across the membrane to its other face in contact with the reactant gas.

Materials for membranes in catalytic membrane reactors must be conductors of oxygen anions, and the materials must be chemically and mechanically stable at the high operating temperatures and under the harsh conditions required for reactor operation. In addition, provision must be made in the reactor for electronic conduction to maintain membrane charge neutrality. Electronic conductivity in a reactor is necessary to maintain charge neutrality permitting anion conduction through the membrane. Electron conduction can be achieved by adding an external circuit to a reactor which allows for current flow. See: U.S. patents 4,793,904, 4,802,958 and 4,933,054 (all of Mazanec et al.).

Electronic conductivity can also be achieved by doping oxygen-anion conducting materials with a metal ion, as illustrated by U.S. patents 4,791,079 and 4,827,071 (both of Hazbun), to generate dual (electrons and oxygen anions) conducting materials. The disadvantage of this approach is that the dopant metal ions can act as traps for migrating oxygen anions, inhibiting the ionic conductivity of the membrane.

Dual conducting mixtures (i.e., mixtures that conduct both electrons and ions) can be prepared by mixing an oxygen-conducting material with an electronically-conducting material to form a composite, multi-component, non-single phase material. Problems associated with this method include possible deterioration of conductivity due to reactivity between the different components of the mixture and possible mechanical instability, if the components have different thermal expansion properties.

The preferred method for obtaining electronic conductivity is to use membrane materials which inherently possess dual conduction property.

As described in U.S. patent applications 08/639,781 and 08/163,620, mixed conducting metal oxides possessing the brownmillerite crystallographic structure or derived from brownmillerite metal oxides can be used to prepare gas-impermeable ceramic membranes for use in membrane reactors for spontaneously separating oxygen from a gas, e.g., from air, on their reducing surface and mediating transfer of this oxygen as oxygen anions to the oxidation surface of the membrane where they can participate in a selected oxidative chemical process. For example, natural gas (predominantly methane) can be spontaneously converted to synthesis gas, a mixture of carbon monoxide (CO) and hydrogen (H_2) which is useful as a feedstock for preparation of liquid fuels.

The reaction to form synthesis gas is a partial oxidation that is written:

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^-$$

Fig. 1 illustrates schematically how this reaction would occur ideally in a ceramic membrane reactor. The membrane of Fig.1 is illustrated as having a reduction catalyst on the reduction surface and a partial oxidation catalyst on the membrane oxidation surface. Fig. 1 illustrates that molecular oxygen (O_2) is reduced at the reducing surface of the membrane to form oxygen anions (O^{2-}) which are conducted across the membrane (due to the presence of an oxygen gradient). O^{2-} at the oxidizing surface of the membrane reacts with methane to give the partial oxidation product CO and H_2 with H_2:CO ratio of 2:1. Higher hydrocarbons can also be partially oxidized to give synthesis gas.

A problem that occurs with ceramic membrane reactors is that the membrane material itself can be catalytically active toward oxygen anion, changing the nature of the oxygen species that are available for reaction at the membrane surface and affecting reaction products. For example, the membrane material may catalyze reoxidation of oxygen anions to molecular oxygen. The membrane then serves to deliver molecular oxygen to the oxidation zone of the reactor. The presence of molecular oxygen can significantly affect the selectivity of a given reaction. For example, reaction of methane with molecular oxygen leads to deep oxidation of methane generating CO_2:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O.$$

A membrane that exhibits no substantial reactivity toward oxygen anions, yet retains ionic and electronic conductivity, i.e. a membrane that is not inherently catalytically active toward oxygen, would provide for better reaction selectivity in a membrane reactor. In this case, reactivity can be determined by choice of an adherent catalyst layer on the oxidation surface of the membrane. By appropriate choice of the adherent catalyst layer a high degree of selectivity for a desired oxidation reaction can be achieved.

The use of a membrane material which has minimal catalytic activity towards oxygen separates the oxygen transport properties of the membrane from its catalytic activity. This allows fine tuning of catalytic activity by catalyst layer choice, in particular it allows control of the surface oxygen species and selection among a variety of oxygen species at the membrane surface O^{2-}, O_2^- (superoxide), O• (radical), peroxo (O_2^{2-}), etc.

SUMMARY OF THE INVENTION

This invention provides a catalytic membrane reactor for partial or full oxidation of reduced species, particularly of hydrocarbons. The reactor comprises a gas-impermeable membrane which exhibits ion conductivity. The membrane is also provided with electronic conduction to maintain membrane charge neutrality. Electronic conduction can be provided by an external circuit or the membrane material can itself be an electronic conductor. The reactor has an oxidation zone and a reduction zone separated by the membrane which itself has an oxidation surface exposed to the oxidation zone and a reduction surface exposed to the reduction zone. The oxidation surface of the membrane is, at least in part, covered with an adherent catalyst layer. The reduction surface of the membrane is optionally provided with an oxygen reduction catalyst. The reactor is also

optionally provided with a three-dimensional catalyst in the oxidation zone of the reactor in close contact with the adherent layer on the oxidation surface of the membrane.

Preferred membranes of this invention are single phase mixed ionic and electronic conducting ceramics. In this case no external electric circuit is required to maintain membrane charge neutrality. To facilitate selective oxidation, preferred membranes are those that exhibit minimal catalytic activity for oxidation of oxygen anions, e.g., are minimally active for reoxidation of oxygen anions to molecular oxygen, on transport of oxygen anion through the membrane. These membranes deliver minimal amounts of molecular oxygen to the oxidation surface of the membrane and to the oxidation zone of the reactor and minimize deep oxidation of hydrocarbons (e.g., CH_4 to CO_2).

Preferred membrane materials of this invention are single-phase materials having the stoichiometric formula:

$$A_{2-x}A'_xB_{2-y}B'_yO_{5+z} \qquad \mathrm{I}$$

where A is an alkaline earth metal ion or mixture of alkaline earth metal ions; A′ is a metal ion or mixture of metal ions where the metal is selected from the group consisting of metals of the lanthanide series and yttrium; B is a metal ion or mixture of metal ions wherein the metal is selected from the group consisting of 3d transition metals, and the group 13 metals; B' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, the group 13 metals, the lanthanides and yttrium; x and y are, independently of each other, numbers greater than or equal to zero and less than or equal to 2; and z is a number that renders the compound charge neutral. The value of z generally is greater than zero and less than 1.0, more preferably z is greater than zero and less than or equal to about 0.5, and most preferably z is greater than zero and less than or equal to 0.3. The exact value of z depends upon the valencies and stoichiometries of A, A', B, and B'. Preferably x is greater than or equal to zero and less than 1 and y is greater than or equal to 1 but less than 2.

The adherent catalyst layer is preferably a mixed ionic and electronic conducting layer. The catalyst of this layer is preferably chosen to facilitate efficient mediation of O^{2-} from the membrane to the chemical species to be oxidized. Alternatively the catalyst is chosen to control the nature of the oxygen species that will interact with the chemical species to be oxidized. A preferred adherent catalyst for facilitating efficient mediation of

O^{2-}, and thus preferred for partial oxidation of hydrocarbons, is a mixed ionic and electronic conducting ceramic having the composition:

$$X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X is Ca, Sr or Ba, Re is a rare earth or lanthanide metal, including yttrium, Z is Al, Ga, In or combinations thereof and Z' is Cr, Mn, Fe, Co, or combinations thereof with $0 \leq a \leq 1$ and $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that renders the composition charge neutral.

The adherent catalyst layer can be formed by catalyst particles with deposited metal to give a mixed conducting (ion and electronic) cermet catalyst. Preferred deposited metals include Ni, Pt, Pd, Rh, Ir, Ag and combinations thereof. Metal can be deposited from about 1wt% to about 50wt% on the supporting catalyst. Ni deposited on a relatively basic mixed conducting support, such as $La_aSr_{1-a}MnO_3$, where $0 \leq a \leq 1$ and particularly where a is $0.7 \leq a \leq 0.9$, is a preferred adherent catalyst for the partial oxidation of methane to synthesis gas.

The adherent catalyst layer can also be a catalyst, such as those listed in Table 1 or 2, which promotes partial oxidation of methane to CO and H_2, promotes oxidative coupling of alkanes, particularly methane to olefins, promotes the oxidative dehydrogenation of alkanes, or which promotes oxygenate production including the partial oxidation of alkanes to alcohols, aldehydes or ketones, the partial oxidation of alkenes to epoxides or the partial oxidation of alkane to anhydrides. Membranes of formula I in combination with an appropriately selected adherent catalyst are useful in catalytic reactor membranes for the listed partial oxidation reactions.

The adherent catalyst layer also provides protection for the membrane material to prevent decomposition under operating conditions.

The optional three-dimensional catalyst can be a packed- or fluidized-bed catalyst, and preferably is a packed-bed catalyst, in close contact with the adherent catalyst layer. This catalyst is selected to promote a desired oxidation reaction. The three-dimensional catalyst can, for example, comprise a metallic catalyst deposited on a support. Preferred metals include Ni, Pt, Pd, Rh, Ir, Ag, and combinations thereof. The support can be an inert oxide or a mixed metal oxide. Inert oxides include alumina. A mixed ionic and electronic conducting material can also be used as the support. The three-dimensional catalyst may be, but need not be, the same material as the adherent catalyst layer.

This invention provides reactors as described above, membranes with adherent catalyst layers and methods of oxidizing reduced species, particularly hydrocarbons, using these reactors and membranes. The invention more specifically provides a catalytic reactor as described above for synthesis gas production from a methane-containing gas.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic drawing illustrating the catalytic membrane reaction leading to formation of synthesis gas from methane.

Figure 2 is a drawing of a single cell membrane reactor (not drawn to scale) with packed-bed catalyst in the oxidation zone.

Figures 3A and 3B are more detailed illustrations of the membrane, adherent catalyst and packed-bed reactor of Fig. 2 and 4.

Figure 4 is an illustrative example of a multiple cell catalytic membrane reactor combining a plurality of reactor membranes of Fig. 2.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to improved catalytic membrane reactors for the selective partial or full oxidation of various reduced chemical species. The reactor, in general, mediates the reaction of a reactant gas stream containing a reduced species, such as a hydrocarbon or partially oxidized hydrocarbon, with an oxygen-containing gas reagent stream to generate reaction products that are oxidized relative to the species initially in the reactant stream. The oxidized products are generated in the reactant stream as catalysis proceeds forming a product stream containing species that are oxidized relative to the reactant species.

The term oxygen-containing gas is used broadly herein to include gases and mixtures of gases in which at least one of the component gases is oxygen or an oxide. The oxygen or oxide component of the gas is capable of being reduced at the reduction surface of the membrane of this invention. The term includes carbon, nitrogen, and sulfur oxides (CO_x, NO_x and SO_x) among others, and gas mixtures in which an oxide is a component, e.g., NO_x in an inert gas or in another gas not reactive with the membrane. The term also includes mixtures of molecular oxygen (O_2) in other gases, e.g., O_2 in air, O_2 in an inert gas, such as He, Ar, etc. In the reactors of this invention, the oxygen-containing gas is passed in contact with the reduction surface of the membrane and the oxygen-containing component of the gas is at least partially reduced at the reduction

surface, e.g., NO_x to N_2. The gas passing out of the reduction zone of the reactor may contain residual oxygen or oxygen-containing component.

The term "reactant gas" is used broadly herein to refer to gases or mixtures of gases containing at least one component that is capable of being oxidized at the oxidation surface of a reactor of this invention. Reactant gas components include reduced species, including, but are not limited to, methane, natural gas (whose major component is methane), gaseous hydrocarbons including light hydrocarbons (as this term is defined in the chemical arts, including alkanes, alkenes, and alkynes) higher hydrocarbons (those with more than 1 carbon atom) and partially oxidized hydrocarbons, such as alcohols. Reactant gases include mixtures of reduced species with inert gases, or mixtures of such components with oxygen-containing species, such as CO, CO_2 or H_2O. The term "oxygen-consuming gas" may also be used herein to describe a reactant gas that reacts with oxygen anions generated at the oxidizing surface of the membrane. In synthesis gas production the reactant gas is a methane-containing gas which can be, among others, methane, natural gas or methane mixtures with alkanes or other hydrocarbons.

The terms "oxygen-containing gas", "reactant gas," "oxygen-consuming gas," any other gas mixture discussed herein includes materials that are not gases at temperatures below the temperature ranges of the pertinent process of the present invention, and may include materials which are liquid or solid at room temperature. An example of an oxygen-containing gas which is liquid at room temperature is steam.

The term "gas-impermeable" as applied to membranes of this invention means that the membrane is substantially impervious to the passage of oxygen-containing or reactant gases in the reactor. Minor amounts of transport of gases across the membrane may occur without detriment to the efficiency of the reactor. It may be that membranes of this invention will allow passage of low molecular weight gases such as H_2. The membranes of this invention conduct oxygen anions and in this sense are permeable to oxygen. The membranes are impermeable to oxygen gas itself.

Referring now to the drawings, where like numbers represent like features, a single-cell catalytic membrane reactor of the present invention may be schematically represented (not drawn to scale), in cross-sectional view, as shown in Fig. 2 and in more detail in Fig. A and B.

Reactor cell (20) comprises a ceramic membrane (2) an adherent catalyst layer (3) and a three-dimensional catalyst (5) enclosed within reactor shell (7). The reactor cell comprises an oxidation zone (4) separated from a reduction zone (6) by the membrane which is gas-impermeable. The membrane is illustrated as a cylindrical closed-end tube, but any shape capable of creating two separate zones would be sufficient. The outer perimeter of the reduction zone is defined by membrane (2) and the outer perimeter of the oxidation zone is defined by the reactor shell (7). The membrane has a reduction surface (8) facing the reduction zone (6), i.e., the inner surface of the tube, and an oxidation surface (9), i.e., the outer surface of the tube facing the oxidation zone (4). Feed tube (10) delivers a reactant gas (12), such as methane, into the oxidation zone (4). Reacted gases (13), including products of oxidation, exit the oxidation zone (4) via at least one exit port (14). An oxygen-containing gas (16), such as air, is delivered into the reduction zone (6) via entrance port (18). Reacted gases (19), such as oxygen-depleted air, exit the reduction zone (6) via at least one exit port (15).

The oxidation surface of membrane (2) is, at least in part, coated with an adherent catalyst layer (3). The catalyst in this layer is chosen as discussed below to promote the desired oxidation reaction. The reactor cell further comprises a three-dimensional catalyst (5) in oxidation zone (4) in contact with adherent catalyst layer (3). The membrane can optional have a layer of an oxygen reduction catalyst (not shown) on its reduction surface to promote reduction of O_2 to oxygen anions.

Oxygen anions (O^{2-}) originate from initial reduction of molecular O_2 (or other oxygen-containing species) on the reducing surface of the membrane and migrate through the membrane to the membrane oxidation surface. The adherent catalyst layer facilitates mediation of oxygen anion (O^{2-}) species from the membrane oxidation surface to the chemical species in the reactant gas undergoing oxidation reactions. The adherent layer can also be selected to control the nature of the oxygen species made available for reaction with the reactant gas. For example, anionic oxygen species can be converted (at least in part) by the adherent catalyst layer into superoxide, oxo, oxygen radical, peroxo or other reactive oxygen species and made available at the catalyst layer for oxidation of reduced species in the reactant gas. The nature of the oxidation reaction that occurs is strongly dependent upon the nature of the reactive oxygen species present at the catalyst layer.

In cases where the oxygen-containing species in the oxygen-containing gas is not O_2 (e.g., NO_2) the reduction surface of the membrane can be coated with a catalyst that promotes the reduction of the oxygen-containing species as described in USSN 08/639,781.

The thickness of the membrane and the adherent catalyst are in general optimized for desired reactor performance. The membrane must be sufficiently thick to provide structural stability and preferably is suitable for long term operation under reaction conditions. The adherent catalyst can, for example, be up to several hundreds of microns thick.

The three dimensional catalyst (5) is separate from, but at least a portion of it is in close contact with the oxidation surface of the membrane and/or adherent catalyst layer on that surface. By being in close contact with the surface or its adherent layer, the oxygen species emerging from the surface or that layer can migrate to the packed-bed or other three-dimensional catalyst yielding a higher surface area for oxidation. In general, the packed-bed is provided as a layer of catalyst particles surrounding the oxidation surface of the membrane. This element of the reactor cell serves to increase production rates and throughput conversions. Fig. 3A and B provide a more detailed illustration of the membrane, adherent catalyst layer and three dimensional catalyst which is exemplified as a packed-bed catalyst.

In the illustrated embodiment of the reactor cell in Fig. 2, the outer surface of the membrane tube is the oxidation surface. Alternative embodiments of the reactor cell include those in which the inner surface of the membrane tube is the oxidation surface and the three dimensional catalyst is positioned within the tube.

The reactor of Fig. 2 is a single cell reactor with a closed-end tubular membrane. The reactor can be implemented as a multiple membrane catalytic reactor as illustrated in Fig. 4.

The reactor (50) of Fig. 4. comprises a plurality of reactor cells (30) of the type described above and depicted in Fig. 2. The cells (30) which comprise closed-end membrane tubes, like those of Fig. 2 are enclosed in a reactor shell (24), and are linked together by manifold (26). An inlet feed tube (28) delivers oxygen-containing gas (22) to reactor cells (30), and oxygen-depleted gas (32) exits the cells via the manifold (26) through exit tube (34). A reactant gas (36) is delivered to the oxidation zone (38) via

reactor shell inlet port (40). Reacted gas containing oxidized products (42) exits the reduction zone (38) via outlet port (44). A three-dimensional catalyst, either a packed-bed, fluidized-bed or related catalyst (not illustrated) is provided in the oxidation zone of this reactor surrounding and in contact with the oxidation surfaces of each of the membranes. The catalyst may be contained within a structure in the reactor oxidation zone surrounding the membrane cells. The three-dimensional catalyst is positioned within the reactor in close contact with the oxidation surfaces of the membranes and the reactant gas, which typically will flow through the three-dimensional catalyst bed.

Preferred membrane materials of this invention are mixed metal oxides having the formula:

$$A_{2-x}A'_xB_{2-y}B'_yO_{5+z} \qquad \text{I}$$

where A, A′, B, B′, x, y and z are as defined above. These mixed metal oxides are derived from brownmillerite and can, themselves, have brownmillerite structure.

A brownmillerite is one of a class of minerals, including mixed metal oxides, having a structure like that of the mineral brownmillerite, Ca_2AlFeO_5. The general formula of a brownmillerite is $A_2B_2O_5$, where the sum of the valences of the A and B atoms is 5. The brownmillerite structure is characterized in having sheets of perovskite-like corner sharing octahedra perpendicular to the crystallographic b axis, separated by layers of single chains of tetrahedra containing ordered vacancies that are parallel to the c axis. Brownmillerite is, thus, a defect perovskite with the oxygen defects in a particular order. Further, in a substituted brownmillerite $AA'BB'O_{5+z}$, where the ratio of B:B' is 1, and where B is a group 13 metal and B' is a 3d transition metal, all the B' ions will substantially occupy octahedral positions and all the B ions will substantially occupy tetrahedral positions in the lattice.

Membrane materials of this invention are oxygen deficient incorporating lattice vacancies which facilitate ion conductivity. Membrane materials are derived from brownmillerites in that the components are combined based on a brownmillerite composition $A_2B_2O_5$ (where A can be A + A' and B can be B + B'). After sintering, single phase membrane materials may be classifiable by XRD or related techniques as having brownmillerite, distorted perovskite or other structure.

A compound of brownmillerite structure is distinct from a perovskite. The two structures can be distinguished by X-ray diffraction (XRD). See: Y. Teraoka, H.-M.

Zhang, S. Furukawa and N. Yamazoe (1985) *Chemistry Lett.* supra. XRD patterns of certain membrane materials of this invention can be fit to a Pcmn cell as expected for the brownmillerite structure. See, P.K. Gallagher, J.B. MacChesney and D.N.E. Buchanan (1964) *J. Chem. Phys.* **41**:2429; C. Greaves, A.J. Jacobson, B.C. Tofield and B.E.F. Fender (1975) *Acta Cryst.* **B31**:641. Table 1 provides lattice parameters for a number of membrane materials of this invention.

A perovskite is one of a class of materials having a structure based on that of the mineral perovskite, $CaTiO_3$. An ideal perovskite structure has a cubic lattice in which a unit cell contains metal ions at each of the corners and in the middle of the cell and oxygen ions at the midpoints of the edges of the cell. The general formula of a perovskite is ABO_3 where A and B are metal ions, the sum of the valences of which are 6. Cable et al. EP 90305684.4 and U.S. 5,306,411 further describe that the radii of the A and B metal ions of a perovskite must conform to the relationship:

$$r_A + r_O = t\sqrt{2}\ (r_B + r_O)$$

where r_A, r_B and r_O are the radii of the A, B and O ions, respectively, and t is a tolerance factor which lies within the approximate range 0.7-1.0.

In a single-phase material, the atoms of the various components of the material are intermingled in the same solid phase. The presence of a single-phase can be assessed by XRD or similar known techniques of structural determination. For example, a single-phase brownmillerite compound is distinguished in that all of the peaks in the XRD can be accounted for by the brownmillerite structure.

More specifically, the membrane materials of this invention are compounds of formula I where the B metal is selected from the group consisting of group 13 metals and mixtures thereof and the B' metal is selected from the group of 3d transition metals or mixtures thereof. Preferred group 13 metals are Al, Ga, and In, and mixtures thereof, with mixtures of Al and Ga being presently more preferred. Transition metal ions more useful for materials of this invention are Co, Ti, V, Cr, Mn, Ni and Fe. Preferred transition metal ions are Cr, Mn, Ni and Fe, with Cr, Mn, and Fe being more preferred and Fe being presently most preferred. Preferred A′ metal ions are La and Y, with La being presently more preferred. Preferred A metal ions are Sr and Ba with Sr being presently more

preferred. In formula I most generally $0 \leq x \leq 2$ and $0 \leq y \leq 2$ and compounds of that formula where $0.2 \leq y \leq 0$ and $1.9 \leq y \leq 2$ are more preferred. Membrane materials of formula I as described are derived from brownmillerite and can include brownmillerites.

Membrane materials of this invention include compounds of formula II.

$$A_{2-x}La_xB_{2-y}Fe_yO_{5+z} \qquad \text{II}$$

where A is an alkaline earth metal ion or mixture of alkaline earth metal ions with A that is Sr and Ba being preferred, B is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, or the group 13 metals, with B that is a group 13 metal being preferred and B that is a mixture of Al and Ga being more preferred; x and y, independently of one another, are numbers greater than or equal to zero and less than or equal to 2, with x greater than or equal to zero and less than or equal to about 1.0 more preferred and y greater than or equal to 1, but less than or equal to 2 more preferred; z is a number that renders the compound neutral, but is typically x/2.

In particular, membrane materials of this invention include materials of formulas IIIA or IIIB:

$$Sr_{2-x}La_xGa_{2-y}C_yO_{5+z} \qquad \text{IIIA}$$

$$Sr_{2-x}La_xAl_{2-y}CyO_{5+z} \qquad \text{IIIB}$$

where C is a 3d transition metal ion and preferably a 3d transition metal ion selected from the group consisting of Fe, Cr or Mn. Compounds of formula IVA and IVB being more preferred:

$$Sr_{2-x}La_xGa_{2-y}Fe_yO_{5+z} \qquad \text{IVA}$$

$$Sr_{2-x}La_xAl_{2-y}Fe_yO_{5+z} \qquad \text{IVB}$$

where x and y are numbers greater than or equal to zero but less than or equal to two. Preferably, x is greater than or equal to zero and less than about 1 and y is greater than or equal to 1, but less than or equal to 2. More preferred compounds of formulas IIIA/IIIB and IVA/IVB have $0.2 \leq x \leq 1.0 \leq y \leq 2.0$.

Membrane materials of this invention also include materials of formula V.

$$A_{2-x}La_xB_{2-y}Fe_yO_{5+z} \qquad \text{V}$$

where A is Sr, Ba, Ca or mixtures thereof and B is Al, Ga, In or mixtures thereof, and x, y and z are as defined above for formula I. Membrane materials include those where x is zero and A is Ba or Ca and B is Ga or Al.

Specific membrane materials of this invention include:

$Sr_{1.6}La_{0.4}Ga_{0.6}Fe_{1.4}O_{5.2}$

$Sr_{1.6}La_{0.4}Ga_{0.8}Fe_{1.2}O_{5.2}$

$Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$

$Sr_{1.7}La_{0.3}GaFeO_{5.15}$

$Sr_{1.6}La_{0.4}Ga_{0.4}Fe_{1.6}O_{5.2}$

$Sr_{1.8}La_{0.2}GaFeO_{5.1}$

$Sr_{1.6}La_{0.4}Al_{0.6}Fe_{1.4}O_{5.2}$

$Sr_{1.6}La_{0.4}Al_{0.8}Fe_{1.2}O_{5.2}$

$Sr_{1.7}La_{0.3}Al_{0.6}Fe_{1.4}O_{5.15}$

$Sr_{1.7}La_{0.3}AlFeO_{5.15}$

$Sr_{1.6}La_{0.4}Al_{0.4}Fe_{1.6}O_{5.2}$

$Sr_{1.8}La_{0.2}AlFeO_{5.1}$

$Sr_{1.6}La_{0.4}Fe_2O_{5.2}$

$Ba_2CeIn_{0.5}Fe_{0.5}O_{5.5}$

$Ba_2Ce_{0.8}Gd_{0.2}In_{0.5}Fe_{0.5}O_{5.4}$

$Ba_2GdIn_{0.5}Fe_{0.5}O_5$

$Ba_2Gd_{0.8}Ce_{0.2}In_{0.5}Fe_{0.5}O_{5.1}$

$Ba_2Gd_{0.5}Ce_{0.5}In_{0.5}Fe_{0.5}O_{5.25}$

$Ba_2Gd_{0.5}Pr_{0.5}In_{0.5}Fe_{0.5}O_{5.25}$

$Ba_2PrIn_{0.5}Fe_{0.5}O_{5.5}$

$Ba_2GdIn_{0.2}Fe_{0.8}O_5$

Catalytic membranes of this invention facilitate reduction of an oxygen-containing gas and transport of oxygen anions across the membrane for interaction with the adherent catalyst, packed-bed catalyst and reactant gas to oxidize a reduced component of the reactant gas. Catalytic membranes are shaped to have two surfaces: a reduction surface and an oxidation surface. The membrane is fabricated sufficiently thick to render it substantially gas-impermeable and mechanically stable to withstand the stresses associated with reactor operation, yet not so thick as to substantially limit the oxygen ion permeation rate through the membrane. Membranes can be fabricated in a variety of shapes appropriate for a particular reactor design, including disks, tubes, closed-end tubes or as reactor cores for cross-flow reactors.

The specific reaction for the production of synthesis gas from methane is:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$$

which is believed mediated by O^{2-} as illustrated in Fig. 1. Other oxidation reactions that can be accomplished using membrane reactors of this invention include: oxidative coupling of alkanes, specifically the oxidative coupling of methane to form ethylene; oxidative dehydrogenation of alkanes, specifically the conversion of alkanes to the corresponding olefins (e.g., ethane to ethylene); various partial oxidation reactions leading to value-added products, specifically the oxidation of alkanes to alcohols, aldehydes or ketones or the oxidation of alkanes to anhydrides.

The adherent catalyst layer is selected to facilitate O^{2-} transport to the reduced species in the reactant gas. Alternatively, the adherent catalyst is selected to promote formation of a given reactive oxygen species for reaction with the reduced species in the reactant gas. Tables 1 and 2 provide a listing of suitable known catalysts with citations to the literature for various hydrocarbon oxidation reactions. The references cited in these two Tables provide details of catalyst composition, structure, preparation and reactivity.

The nature of the surface oxygen species that interact with the reactant gas will depend strongly on the adherent catalyst. In turn, the type of oxidation reaction that occurs (or dominates) depends upon the nature of the oxygen species that interact with the reactant gas.

The formation of carbon oxides, CO_2 in particular, is favored by the presence of species which promote the formation of metal oxo (M=O) species, either by direct conversion of oxygen ions to the oxo form or by rupture of peroxo (O-O) bonds. Compositions containing first row transition metal ions, such as Co^{2+}, Ni^{2+}, or Fe^{2+} in a weakly basic matrix are expected to promote the formation of monoatomic surface oxygen species and facilitate oxygen transfer to hydrocarbons, for example partial oxidation of methane to CO. Dimeric oxygen species such as the peroxo (M-O-O-M) or superoxide (O_2^-) are effective in catalyzing hydrogen abstraction. Formation of dimeric surface species is favored by the presence of relatively non-reducible ions of S, P, and other types of metals (e.g., Ce^{4+}, Pb^{4+}, Bi^{3+}) in a strongly basic matrix (i.e., containing high concentrations of Sr^{2+} or Ba^{2+}, for example). This type of catalyst will promote hydrocarbon coupling reactions.

As indicated above, preferred adherent catalyst of this invention can be selected from mixed ionic and electronic conducting ceramics of the formula:

$$X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where A is Ca, Sr or BA, Re is a rare earth or lanthanide metal, including Yttrium, Z is Al, Ga or In and Z' is Cr, Mn, Fe or Co with a and b numbers such that $0 \leq a \leq 1$ and $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that renders the composition charge neutral.

Cermet (a composite between a ceramic and a metal) catalysts of formula:

$$M/X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X, Re, Z and Z', a, b and c are as defined immediately above and M is a metal chosen to promote the desired oxidation reaction are also preferred for use as adherent catalysts. Metals for cermet catalysts are preferably selected from Ni, Pt, Pd, Rh, Ir or Ag, Cr, V, Mo or W. The weight percent of metal to mixed conducting catalyst can vary from 1 to about 50%. Preferred content of metal to mixed conducting catalyst is from about 5wt% to about 20wt%. The oxidation products obtained will depend upon the support and the metal chosen. Silver, for example, favors oxygen evolution. However, when silver is incorporated onto a very basic support (i.e., one containing a high concentration of Sr or Ba), the formation of surface superoxide species and hydrogen abstraction processes are favored. Ni favors partial oxidation of hydrocarbons, as illustrated in the examples herein, when incorporated onto a moderately basic support, such as $La_{0.8}Sr_{0.2}MnO_3$.

The platinum group of metals (Pt, Pd, Rh, or Ir) on oxide supports will promote different reactions dependent upon choice of support and process variables such as residence time of reactant gas in the reactor. Short residence times favor dehydrogenation products when the metal is supported on a moderately basic to neutral support. Longer residence times with platinum group metals on basic supports tend to favor deep oxidation.

In order to maintain the mechanical integrity of the membrane/adherent catalyst combination, it is preferred to select lattice substituents that impart refractory properties such that a stable solid state interface is formed between the mixed conducting adherent catalyst and the mixed conducting membrane. Using substituents that are similar in both

the adherent catalyst layer and the membrane will prevent detrimental solid-state reaction or diffusion between the catalyst layer and the membrane.

The membrane is optionally provided with an oxygen reduction catalyst such as $La_aSr_{1-a}Co\ O_{3-x}$ where $a \leq 0 \leq 1$ and x is a number such that the compound is charge neutral, a is preferably 0.5 or more, and more preferably, a is 0.7 to 0.9; Ag, Pt or Pd metals (e.g., as metal deposited on the membrane); or catalysts of the formula: $ACo_{1-x}M_xO_{3-\delta}$, where A is Ca, Sr, Ba or combinations thereof, x is a number less than 1 and δ is a number that renders the catalyst charge neutral. M is a metal ion with empty metal e_g orbitals and filled metal t_{2g} orbitals, with preferred first row transition metal ions being those of Fe, Co and Ni (e.g., Fe^{2+} and Co^{3+}). Oxygen reduction catalysts can also include those with a coating, e.g., a metal (about 1 wt% - about 50 wt%) on LSC ($La_{0.8}Sr_{0.2}CoO_{3-x}$). Preferred metal-coated oxygen reduction catalysts have about 5wt% to about 20wt% metal. Preferred metals are the platinum group metals (Pt, Pd, Rh or Ir) and more preferred metals are Pt and Pd. Preferred membranes are provided with an oxygen reduction catalyst.

Catalyst layers or coatings can be introduced onto and adhered to membrane surfaces by a variety of methods. For example, a slurry of the catalyst powder in an organic solvent can be prepared and coated on to the membrane surface. The thickness of the layer or coating can be adjusted by varying the amount of slurry coated on the membrane or by adjusting the amount of catalyst in the slurry. The coated membrane is annealed at an appropriately high temperature to remove residual solvent.

Preferred reactors of this invention are provided with a three-dimensional catalyst in the oxidation zone in contact with the adherent catalyst layer. The three-dimensional catalyst can be provided as a packed-bed, moving-bed, entrained-bed or fluidized-bed catalyst. Dependent upon particular catalyst type, catalyst particles can vary in shape (spherical, irregular, cylindrical, etc.) and vary in size from microns to millimeters in size.

A preferred three-dimensional catalyst is a packed-bed catalyst composed of particles of catalyst surrounding the membrane at the oxidation surface. The packed-bed component of the reactor can serve to significantly increase production rates and throughput conversion in a given membrane reaction. By being in close contact with the adherent layer, the oxygen species at the adherent layer can migrate to this packed-bed yielding a higher surface area for reaction.

The three-dimensional catalyst is selected, as is the adherent layer, to promote the desired oxidation reaction. The catalyst can be a metal on inert oxide catalyst, such as Ni on Al_2O_3 or other inert support. Alternatively, the catalyst can be a metal supported on a mixed ionic and electronic conducting material, such as Ni on $La_{0.8}Sr_{0.2}MnO_3$. The metal can be present in the catalyst from about 1wt% to about 50wt%. The catalyst in the packed-bed can comprise the same (or different) catalytic material as the adherent catalyst layer and can be chosen dependent upon application and reaction conditions from the catalysts listed in Tables 1 and 2.

Membranes with adherent catalyst layer and optionally with oxygen reduction catalyst layer can be characterized by several measurable properties, including total conductivity, anion conductivity and oxygen permeation rates as well as by their performance in a catalytic membrane reactor for promoting a given reaction. Methods for measuring conductivity and oxygen permeation rates are known in the art and exemplary methods are provided in PCT/US96/14841. For example, a 0.97mm thick tube of $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ coated on both surfaces with $La_{0.8}Sr_{0.2}Co\ O_{3-x}$ where x is a number that renders the compound charge neutral exhibited an oxygen permeation rate of 0.21 ml/min. cm^2 when measured at 900°C in a reactor with the reduction zone exposed to air and the oxidation zone exposed to He.

The catalytic reactor membranes specifically exemplified in the following examples are run at 900°C for production of synthesis gas from methane. Dependent upon the type of reaction catalyzed membrane reactors of this invention can be run over a relatively wide range of temperatures from about 500°C to about 1100°C. The specific temperature and flows of reactant gas and oxygen-containing gas are optimized for a given reaction and membrane material/catalyst. The temperature must be sufficiently high to facilitate useful oxygen anion flux through the membrane without significant product decomposition and without significant damage to the membrane and catalyst materials.

The membranes, adherent catalyst, optional oxygen reduction catalyst and optional three-dimensional catalyst can be readily adapted to a variety of membrane reactor designs following the guidance provided herein.

The following examples are illustrative of the invention and are in no way intended to be limiting.

EXAMPLES

Example 1: Synthesis Gas Production in a Reactor with and without an Adherent Catalyst Layer.

Closed-one-end tubular membranes were fabricated from a single-phase material having the formula: $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$. Powders of this composition were prepared using standard solid state synthetic techniques, particularly as described in PCT/US96/14841 and Example 5 herein. Single-phase powders were pressed into a tubular shape by isostatic pressing and subsequently sintered yielding dense and strong tubular membranes. Care must be taken to assure, by repeated grinding and sintering steps, if needed, that the material is single phase prior to forming tubes by isostatic pressing.

The insides (reduction surface) of the tubular membranes were coated with a layer of $La_{0.8}Sr_{0.2}CoO_3$ (LSC) serving as an oxidation/reduction catalyst. Alternatively, the reduction surface can be coated with a metal on an oxidation/reduction catalyst, e.g., Pd 5wt% on LSC.

The outer surface of one tubular membrane was coated with Ni(20wt%) on $La_{0.8}Sr_{0.2}MnO_3$. This catalyst served as an adherent catalyst layer on the oxidation surface of the membrane.

Tubular membranes with and without the adherent catalyst layer were compared in a synthesis gas reactor, like that of Fig. 1. In both cases, the reactor was provided with a packed-bed of Ni(5wt%) on Al_2O_3 in the oxidation zone of the reactor. In each case, air was used as the oxygen-containing gas passed through the inside of the tubular membranes and a mixture of 80% (volume) methane in helium was used as the reactant gas passed outside the tubular membrane through the packed-bed catalyst. Both reactors were operated at 900°C. Table 3 summarizes the results of this comparison.

TABLE 3: Comparison of Results Obtained for $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ Closed-one-end Membrane Tube Reactors at 900°C with and without an Adherent Catalyst Layer.

Reactor Configuration	Production Rate ($ml/min\text{-}cm^2$)	H_2:CO	CO Selectivity (%)	Throughput Conversion (%)
No Adherent Catalyst Layer	0.16	2.4	86	<1
Ni(20%wt)on $La_{0.8}Sr_{0.2}MnO_3$ Adherent Catalyst Layer	44.9	1.8	97	77

The membrane reactor in which there was no adherent catalyst layer exhibits essentially no activity towards partial or deep oxidation of methane, even in the presence of a packed-bed catalyst. The membrane reactor in which there is an adherent catalyst layer on the oxidation surface of the membrane is extremely active towards the partial oxidation reaction with high production rates of synthesis gas and high throughput conversions without sacrificing selectivity as evidenced by the high CO selectivity and H_2:CO ratio.

Example 2: Synthesis Gas Production in a Reactor with and without a Packed-Bed Catalyst

Closed-one-end tubular membranes were fabricated from a single-phase material having the formula: $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ as in Example 1.

The insides of the tubular membranes were coated with $La_{0.8}Sr_{0.2}CoO_3$ serving as an oxidation reduction catalyst. The outer surfaces of the tubular membranes were coated with an adherent catalyst: of Ni(20wt%) on $La_{0.8}Sr_{0.2}MnO_3$.

Tubular membranes were compared in a synthesis gas reactor, like that of Fig. 1. One reactor was provided with a packed-bed of Al_2O_3 pellets which had been coated with powder of Ni(10wt%) on $La_{0.8}Sr_{0.2}MnO_3$ in the oxidation zone of the reactor. In each case, air was used as the oxygen-containing gas passed through the inside of the tubular membranes and a mixture of 80% (volume) methane in helium was used as the reactant gas passed outside the tubular membrane through the packed-bed catalyst. Both reactors were operated at 900°C. Table 4 summarizes the results of this comparison.

TABLE 4: Comparison of Results Obtained for $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ Closed-one-end Membrane Tube Reactors at 900°C with and without a Packed-Bed Catalyst.

Reactor Configuration	Production Rate ml/min-cm^2)	H_2:CO	CO Selectivity (%)	Throughput Conversion (%)
No Packed-Bed Catalyst	2.55	2.0	50	13
Packed-Bed Ni(10%wt)on $La_{0.8}Sr_{0.2}MnO_3$ on Al_2O_3	11.04	1.9	97	39

The membrane reactor having the packed-bed catalyst showed dramatically higher productivities, throughput conversions and CO selectivity without loss of H_2 selectivity as evidenced by the high H_2:CO ratio.

Example 3: Synthesis Gas Production in a Reactor with different Adherent Layer Catalyst

Closed-one-end tubular membranes were fabricated from a single-phase material having the formula: $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ as described in Example 1.

The insides of the tubular membranes were coated with $La_{0.8}Sr_{0.2}CoO_3$ serving as an oxidation reduction catalyst.

The outer surface of one tubular membrane was coated with $La_{0.8}Sr_{0.2}MnO_3$. The outer surface of a second tubular membrane was coated with Ni(20wt%) on $La_{0.8}Sr_{0.2}MnO_3$. These catalysts served as adherent catalyst layers on the oxidation surface of the two membranes.

Tubular membranes with different adherent catalyst layers were compared in a synthesis gas reactor, like that of Fig. 1. In both cases, the reactor was provided with a packed-bed of Ni(5wt%) on Al_2O_3 in the oxidation zone of the reactor. In each case, air was used as the oxygen-containing gas passed through the inside of the tubular membranes and a mixture of 80% (volume) methane in helium was used as the reactant gas passed outside the tubular membrane through the packed-bed catalyst. Both reactors were operated at 900°C. Table 5 summarizes the results of this comparison.

TABLE 5: Comparison of Results Obtained for $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ Closed-one-end Membrane Tube Reactors at 900°C with Different Adherent Catalyst Layers.

Reactor Configuration	Production Rate (ml/min-cm^2)	H_2:CO	CO Selectivity (%)	Throughput Conversion (%)
$La_{0.8}Sr_{0.2}MnO_3$ Adherent Catalyst Layer	23.0	1.8	99	44
Ni(20%wt)on $La_{0.8}Sr_{0.2}MnO_3$ Adherent Catalyst Layer	30.4	1.8	99	68

Both membrane reactor exhibit high productivities and throughput conversions with high selectivities. The reactor utilizing Ni(20%wt) on $La_{0.8}Sr_{0.2}MnO_3$ as the adherent catalyst layer has approximately 30% higher productivity. This indicates that the adherent catalyst layer not only operates as an oxygen catalyst, but also can be used to promote the desired oxidation reaction.

Example 4: Effectiveness of an Adherent Catalyst Layer for Protection of the Membrane Surface

A closed-one-end tubular membrane were fabricated from a single-phase material having the formula: $Sr_{1.7}La_{0.3}Ga_{0.6}Fe_{1.4}O_{5.15}$ as in Example 1. The inside of the tubular membranes were coated with $La_{0.8}Sr_{0.2}CoO_3$ serving as an oxidation reduction catalyst. A portion of the outer surface of the tubular membrane was coated with an adherent catalyst: Ni(40wt%) on $La_{0.8}Sr_{0.2}MnO_3$. The remaining portion of the membrane surface was left uncoated. No packed-bed catalyst was used in this experiment. A reactor containing the partially coated tubular membrane was run under the same conditions for synthesis gas reaction as in Examples 1-3. The reactor was run for one year after which it was voluntarily terminated. A white coating had formed on the oxidation surface of the membrane that had not been coated with adherent catalyst. The other portion of the membrane surface that had been coated did not show this white coating. Subsequent energy dispersive spectroscopy and X-Ray photoelectron spectroscopic analysis of the white powder identified it as $SrCO_3$. This compound likely forms as a result of the reaction of SrO with CO_2. This result indicates that the membrane material is segregating into components. No evidence of this reaction is observed in the region of the reactor that

is coated. This suggests that the addition of Mn or other transition metals such as Cr, V or Ti through the adherent layer prevents Sr segregation in the membrane. Alternatively, higher La content or doping with other lanthanide metals into the membrane material can also ameliorate segregation.

Example 5: Membrane Fabrication

All membrane materials were prepared from mixtures of the appropriate metal oxide(s) and metal carbonate(s) in the desired stoichiometries. Powders were placed in a small polyethylene container with an equal amount, by volume, of isopropyl alcohol. Several cylindrical yttria-stabilized zirconia (YSZ) grinding media were also added to the container. The resulting slurry was mixed thoroughly on a ball mill for several hours. The alcohol was then allowed to evaporate yielding a homogeneous mixture of the starting materials.

This homogeneous mixture was calcined to obtain the desired phase. Powders were placed in alumina crucibles and fired at temperatures up to about 1450°C for 12 h in atmosphere. Upon cooling, the powders were ground to -100 mesh with a mortar and pestle. The ground powder was then analyzed by X-ray diffraction (XRD)to verify that the proper phase had been formed. Calcining was repeated if necessary until the desired single-phase material was obtained. If repeated calcination was required, the powders were thoroughly milled in between calcinations. XRD was performed using a Rigaku Miniflex X-Ray Spectrometer, Model CN2005 using $Cu_{K\alpha}$ radiation (λ = 1.542 Å). Scan speed was 2°(2θ)/min for this preliminary XRD and 0.5°(2θ)/min for determination of lattice parameters.

Before pressing and sintering, the particle size of the powders was reduced by attrition. A Union Process Model 01 attritor with a YSZ tank and YSZ agitator arms was used for this process. In a typical attrition, about 1.5 lbs of 5 mm, spherical YSZ grinding media were placed in the tank. Isopropyl alcohol (about 120 mL) was then added to the tank followed by about 100 g of the -100 mesh powder. The powder was again reduced by attrition for 1 h, after which the alcohol was allowed to evaporate. XRD was again performed on the powder to ensure that the attrition procedure did not cause decomposition. No decomposition was observed for any materials. The XRD patterns showed considerable peak broadening, indicative of small particles. The particle size at this stage was believed to be submicron.

After attrition, powders were pressed into disks and sintered. The powder was mixed with a binder, e.g. a standard ceramic binder, such as Ceracer C640 (Shamrock), which is a polyethylene wax, with a mortar and pestle until a homogeneous mixture was obtained. Another suitable ceramic binder is methyl-cellulose. The binder/powder mixture (about 1 g) was placed in a 12.5 mm diameter die. The mixture was then pressed into disks at 15,000 psi for several minutes. These "green" disks were then placed into an Al_2O_3 crucible for sintering. Disks were packed with powder of the same material to ensure that the disks did not react with the crucible or sinter together. Disks were sintered in the crucible in atmosphere for 4 h at the appropriate sintering temperature for a given material from about 1300°C to about 1450°C to obtain sintered disks preferably of ≥ 90% theoretical density. Sintering temperature for a given material was determined empirically as is known in the art. Sintering temperatures used for representative materials are listed in Table 1. Typical ramp rates during sintering were 3°C/min for both heating and cooling cycles.

To form membranes of this invention, metal oxides or carbonates were combined in the desired stoichiometric ratio. For example, for $Sr_{1.2}La_{0.8}GaFeO_{5.4}$, 60.0 g La_2O_3, 40.7 g $SrCO_3$, 21.6 g Ga_2O_3 and 8.3 g Fe_2O_3 were combined. The resulting powder mixture was repeatedly calcined until it was single-phase material at temperatures up to 1400°C. The resulting single-phase material was pressed into a disk and sintered at 1450 °C.

After sintering, one face of the sintered disk was examined by XRD to ensure that no decomposition had occurred. Additionally, an XRD pattern at a scan rate of 0.5 °C (2θ)/min was obtained on the powder prepared under identical conditions to determine lattice parameters. Lattice parameters were determined by fitting the observed pattern as is known in the art using commercially available Microindex software (Materials Data, Inc., Livermore, CA). See C. Greaves et al. (1975) supra.

Membrane materials can also be shaped into tubes and closed-one-end tubes by isostatic pressing using appropriately shaped molds .

A commercial isostatic press (Fluition CP2-10-60) was employed to form closed-one-end tube membranes. This press is capable of operation to 54,000 psi to form tubes of ~ 4 cm outer diameter and 10 cm in length. Powder was prepared and reduced in particle size as discussed above. Binder (3%, C640 binder) was added to the powder. A

rubber mold was fabricated in the desired outer shape of the tube. A small amount of powder sufficient to form the top end of the closed-end tube was introduced into the mold. A mandrel having the shape of the inner surface of the tube was then inserted into the mold.

A plug funnel was inserted into the top of the mold to allow powder to be added evenly around the mandrel. In particular, the funnel employed was designed so that it fit over the end of the mandrel and centered the mandrel in the mold. Powder was then poured into the mold via the funnel with vibration to ensure even packing. After packing, the mold was plugged and deaerated through the plug. The mold was inserted into the press. Pressure of 30,000 psi to about 40,000 psi was applied to the mold for about 2m. After pressurization, the mold was removed and the green tube was removed from the mold. Very high green densities up to 80%, as measured by the Archimedes method, were obtained.

Green closed-one-end tubes were sintered by placing the tubes (closed-one-end down) in a crucible and inert small diameter beads of yttria-stabilized zirconia (commercially available) were placed around the tubes to keep the tubes straight during sintering. XRD of the tube surface after sintering indicated that no reaction had occurred between the beads and the tube. Straight closed-end tubes of sintered density typically between about 90% to 95% were prepared using this method.

Those of ordinary skill in the art will appreciate that the objects and practice of this invention can be accomplished without resort to the specific reactors, membranes, catalysts, reagents and reactants disclosed herein. Further, it will be appreciated that techniques for preparation of membranes, adherent catalysts, and three-dimensional catalysts and reactor designs and operation other than those specifically described herein can be employed without deviating from the spirit and scope of this invention.

TABLE 1: **Partial Oxidation, Steam Reforming and CO_2 Reforminig Catalysts**

		Ref. No.
A)	**Perovskites and Related Phases** 1. Cobalt containing perovskites $LnCoO_3$ where Ln is a rare earth.	1
	2. Titanate Perovskites Ni on $Ca_{1-x}Sr_xTiO_3$. (Particularly under reducing conditions.)	2
	Ni on $Ca_{1-x}Sr_xTi_{1-y}Ni_yO_3$.	3
	$Ca_{1-x}Sr_xTiO_3$ containing Cr, Fe, Co or Ni	4, 5
	3. Ni based perovskites	6
	$LaNiO_3$, $La_{0.8}Ca(\text{or } Sr)_{0.2}NiO_3$, $LaNi_{1-x}Co_xO_3$ These are mixed conductors	6
	$LaNiO_x$, $LiNiLaO_x$	7
	$LaNiO_3$ and $LaNiAl_{11}O_{19}$	8
	NiO-LnO 1:1 (Ln = lanthanide)	9
	4. Miscellaneous Perovskites a. $Ba_3NiRuTaO_9$, can be a mixed conductor	10
	b. La-M-O where M = Co, Cr, Ni, Rh	11
	c. Ba-Pb, Ba-Bi and Ba-Sn Perovskites	12
	5. Undefined Perovskites	13, 14, 15
B)	**CeO_2 and Metal-Supported on CeO_2** Doped cerias are ionic conductors and under reducing conditions can become electronic conductors as well.	
	1. CeO_2 in a redox cycle	16
	2. Ru or Ir on samaria-doped ceria	17
	3. Pt black on CeO_2	18
	4. Rh on CeO_2	19
C)	**Yttria-Stabilized Zirconia Support** YSZ is an oxide ion conductor. Doping may produce electronic conductivity under reducing conditions.	
	1. Ru on YSZ	20
	2. Ni on YSZ	21
	3. Rh on YSZ	22, 23

D)	**Partial Oxidation in a Fuel Cell or Electrochemical Reactor** Although not a membrane, an oxide ion based fuel cell delivers oxygen (or oxide ions) to the partial oxidation surface similar to mixed conducting membranes of this invention. Therefore, the catalysis is applicable.		
	1.	Pt electrocatalyst	
		a. YsZ electrolyte	24
		b. Undefined electrolyte	25
	2.	Ni electrocatalyst	
		a. on doped $LaGaO_3$ electrolyte	26
		b. on YSZ	27
	3.	Rh electrocatalyst on YSZ electrolyte	28
	4.	Fe on YSZ	29, 30, 31
	5.	Rh on YSZ	32, 33
	6.	Pd on YSZ	34
	7.	Ag on YSZ	35
	8.	CeO_2 and Rh/CeO_2 on YSZ	36
	9.	$YBa_2Cu_3O_x$ on YSZ. This is a mixed ionic/electronic conductor but not stable under reducing conditions	37
E)	**Metals on Titanium Oxide** If metals form compounds with the titanium oxide, then titanates with mixed ionic and electronic conductivity can develop.		
	1.	Ni on TiO_2	38, 39
	2.	Ir on TiO_2	40
	3.	Ru on TiO_2	41
	4.	Pd on TiO_2	42
F)	**Miscellaneous**		
	1.	Rare Earth Transition Metal Pyrochlores - Pyrochlores are known ionic and electronic conductors	43

2.	Rh Black - an Rh oxide which can exhibit mixed conductivity	44
3.	Pt - Pt is a good oxygen catalyst	45
4.	Mo and W Carbides	46

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TABLE 2: CATALYSTS FOR VARIOUS OXIDATION REACTIONS

	Ref. No.
A) Oxidative Coupling of Methane (OCM) **1) Alkaline Earth Compounds (Mg, Ca, Sr and Ba Oxides)** Each material can be used on its own, or doped, or with co-catalysts.	
a) MgO and $MgSO_4$	47
b) Lithium aluminate/MgO with or without an MoO_3 co-catalyst	48
c) MgO doped with rare earths Nd_2O_3	49
La_2O_3 with CaO and BaO	50
Sm_2O_3	51, 52
La_2O_3	53
d) Alkali metal promoted Li, Na, K, Rb and Cs promoted,	54
Li and Li/CeO promoted	55, 56
Li and Li/Sn promoted	57
Li promoted	58, 59, 60, 61
K/Ni promoted CaO and MgO	62
Li and transition metals	63, 64
Li/MgO in membrane reactor	65
e) Transition Metal Doped Ni	66
f) Calcined coral sands	67
g) $SrCO_3$ on aluminosilicate	68
h) Sr with Li on SiO_2	69
2) Rare Earths and Rare Earth Compounds	
a) Rare earth oxides	70, 71, 72
in membrane reactors	73, 74
b) $BaLa_2O_4$	75

	c)	Pr_2O_3	76
	d)	Sm_2O_3 on Al_2O_3	77
	e)	La oxide, sulfate and phosphate	78
	f)	with alkaline earths Li_2O, CaO and MgO doped	79
		CaO	80
	g)	Halides $BaCO_3/LaOBr$	81
		LaF_3/SrO and SrF_2/La_2O_3	82
	h)	Na promoted	83
	i)	$Sm_2Sn_2O_7$	84
3)	**Molybdate and Tungstate Compounds**		
	a)	Alkali promoted $MnMoO_4$	85, 86, 87, 88, 89
		LiCl and Na_2MoO_4	90
	b)	WO_4 on SiO_2 with Na	91
4)	**Zirconia-Based Catalysts**		
	a)	Alkali treated	92, 93
5)	**Ag-Based Catalysts**		
	a)	with sodium phosphate promoter	94
	b)	within electrochemical cell	95, 96
6)	**Lead-Based Catalysts**		
	a)	PbTiO3 with or without NaCl	97
	b)	$PbAl_2O_4$	98
	c)	PbO in Pb or alkali salt melts	99
	d)	Pb in hydroxyapatite	100, 101
	e)	Pb in membrane reactor	102, 103
7)	**Transition-Metal-Oxide-Based Catalysts**		
	a)	Fe_2O_3 with B_2O_3 and NaCl	104
		With LiCl	105

b) $SrCoO_3$	106
c) Pervoskite ion conductors $La_{0.8}Sr_{0.2}CoO_3$ and $SrCo_{0.8}Fe_{0.2}O_3$	107
Perovskites in membrane reactors	108
Doped La/Mn perovksites	109, 110 111
d) Zn on Al_2O_3	112, 113
8) **Bismuth- and Antimony-Based Catalysts**	
a) $Bi_2Sn_{2-x}Bi_xO_{7-x/2}$	114
b) Y_2O_3 doped Bi_2O_3 ion conductor	115
c) $Ba2Sb(La_{0.5}Bi_{0.5})O_6$ and $Ba_4SbTa_2LiO_{12}$	116
B) **Oxidative Dehydrogenation of Alkanes** Including the conversion of alkanes such as ethane, propane and butane into the corresponding olefins ethylene, propylene and butylene.	
1) **Vanadium-Based Catalysts**	
a) Vanadia with MgO Mg-vanadate	117
Mg-vandate phases	118
V-Mg-O in membrane reactor	119, 120
V_2O_5/MgO	121
Magnesium-vanadium	122
Vanadium-magnesium oxide	123
$Mg_3V_2O_8$	124
Vanadium magnesium phases for ethylbenzene	125
b) Other supports Vanadium on metal and aluminophosphates	126, 127 128, 129
Vanadium-containing zeolites	130
V_2O_3 on gamma-Al_2O_3	131,132
Vandium oxide on $BaCO_3$	133
vanadium on Al_2O_3, sepiolite, hydrotalcite	134
Niobia supported vanadia	135

		V_2O_5/TiO_2 with or without alkali metal additives	136
		Vanadia on Al_2O_3 with or without K	137
		V_2O_5/TiO_2	138
		V_2O_5/TiO_2 and $(VO)_2P_2O$	139
		Vanadium on $AlPO_4$	140
	c)	Other compounds $Mg_4V_2Sb_2O_x$	141-142
		Rare earth vandates	143
		Iron containing bismuth molybdovanadate	144
		$(VO)_2P_2O_7$	145, 146
		Vanadium containing silicalite	147
2)	**Molybdenum-Based Catalysts**		
	a)	Compounds	148
		$MgMoO_4$-MoO_3	149
		Cs, V, Mn added to $H_3PMo_{12}O_{40}$	150
		$Cs_{2.5}Cu_{0.08}H_{3.3}PV_3Mo_9O_{40}$	151
		Nickel molybdate with or without alkali metal promoters	152
		Magnesium molybdate	153
		Metal molybdate	154
		$Cr[PMo_{12}O_{40}]$	155
	b)	Miscellaneous molybdenum-based	156
3)	**Noble Metal Catalysts**		
	a)	Silver supported on Al_2O_3 in fluidized bed and monolith	157
	b)	Platinum, Rhodium, Palladium Pt-Sn and Pt-Cu on ceramic monoliths	158
		Pt/Rh gauze	159
		Pt, Pd, Rh on ceramic monolith	160, 161, 162

	supported on Al_2O_3	163
4)	**Transition Metal Compounds**	
	$MgFe_2O_4$	164
	$La_{1-x}Sr_xFeO_{3-y}$ perovskite and ion conductor	165
	Cr-Mn composition	166
	Cu-Th oxide	167
	Transition metals in zeolite ZSM-5	168
	MFI-Ferrisilicate	169
	Mn and Cr oxides on alumina or silica	170
	Fe-Cr-bimetallosilicate	171
	Chromia-alumina in membrane reactor	172
5)	**Antimony and Bismuth Compounds**	
	Iron antimony oxide	173
	Layered bismuth chlorides $SrBi_3O_4Cl_3$ and $Ksr_2Bi_3O_4Cl_6$	174
	Antimony containing Keggin type heteropolyoxomolybdates	175
6)	**Halide Containing**	
	Metal oxide/metal fluoride	176
	BaF_2 doped LaOF	177
	Organochlorine additives on Sm_2O_3 and MgO	178
7)	**Boria Containing**	
	Alumina-boria	179
	Boria-alumina	180
	Boria on yttria-stabilized zirconia	181
8)	**Li/MgO**	182
	In membrane reactor	183

C) Oxygenate Production Including reactions such as methane to formaldehyde or methanol, ethylene or propylene to the corresponding epoxide or butane to maleic anhydride.	
Ferric molybdate	184
MoO_3-SiO_2	185, 186, 187
Alakli metal cations with MoO_3-SiO_2	188
V_2O_5-SiO_2	189, 190

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We claim:

1. A catalytic membrane reactor which comprises:

   an oxidation zone and a reduction zone separated by a gas-impermeable membrane which has an oxidation surface in contact with the oxidation zone and a reduction surface in contact with the reduction zone;

   an adherent catalyst layer on the oxidation surface of the membrane;

   a three-dimensional catalyst in the oxidation zone

   wherein the membrane is a single-phase mixed ionic and electronic conducting ceramic, and the catalyst layer and the three-dimensional catalyst promote an oxidation reaction.

2. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst promote a partial oxidation of a hydrocarbon.

3. The catalytic membrane reactor of claim 1 wherein the membrane ceramic has the formula:

$$A_{2-x}A'_xB_{2-y}B'_yO_{5+z}$$

   where A is an alkaline earth metal ion or mixture of alkaline earth metal ions; A′ is a metal ion or mixture of metal ions where the metal is selected from the group consisting of metals of the lanthanide series and yttrium; B is a metal ion or mixture of metal ions wherein the metal is selected from the group consisting of 3d transition metals, and the group 13 metals; B' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, the group 13 metals, the lanthanides and yttrium; x and y are, independently of each other, numbers greater than or equal to zero and less than or equal to 2; and z is a number that renders the ceramic material charge neutral.

4. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer is a mixed ionic and electronic conducting ceramic having the formula:

$$X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X is Ca, Sr, Ba or mixtures thereof, Re is a rare earth or lanthanide metal, including Yttrium, or mixtures thereof; Z is Al, Ga, In or mixtures thereof; Z' is Cr, Mn, Fe, or Co or mixtures thereof; $0 \leq a \leq 1$, $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that render the composition charge neutral.

5. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer is a mixed ionic and electronic conducting ceramic having the formula:

$$M/X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X is Ca, Sr, Ba or mixtures thereof, Re is a rare earth or lanthanide metal, including Yttrium, or mixtures therof; Z is Al, Ga, In or mixtures thereof; Z' is Cr, Mn, Fe, or Co, or mixtures thereof; $0 \leq a \leq 1$, $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that renders the composition charge neutral; M is a metal selected from Ni, Pt, Pd, Rh, Ir, Ag, Cr, V, Mo, W or mixtures thereof wherein the weight percent of metal to mixed conducting catalyst ranges from about 1wt% to about 50wt%.

6. The catalytic membrane reactor of claim 1 further comprising an oxygen reduction catalyst layer on the reduction surface of the membrane.

7. The catalytic membrane reactor of claim 6 wherein the oxygen reduction catalyst is $La_aSr_{1-a}CoO_{3-x}$, where a is a number such that $0 \leq a \leq 1$ and x is a number such that the compound is charge neutral.

8. The catalytic membrane reactor of claim 6 wherein the oxygen reduction catalyst is a metal selected from Ag, Pt or Pd.

9. The catalytic membrane reactor of claim 6 wherein the oxygen reduction catalyst is a catalyst of the formula: $ACo_{1-x}M_xO_{3-\delta}$, where A is Ca, Sr, Ba or combinations thereof, x is a number less than 1 and δ is a number that renders the catalyst charge neutral; M is a metal ion with empty metal e_g orbitals and filled metal t_{2g} orbitals.

10. The catalytic membrane reactor of claim 1 wherein the membrane ceramic has the formula:

$$A_{2-x}La_xB_{2-y}Fe_yO_{5+z}$$

where A is an alkaline earth metal ion or mixture of alkaline earth metal ions, B is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, or the group 13 metals; x and y, independently of one another, are numbers greater than or equal to zero and less than or equal to 2, and z is a number that renders the ceramic charge neutral.

11. The catalytic membrane reactor of claim 1 wherein the three-dimensional catalyst is a packed-bed catalyst.

12. The catalytic membrane reactor of claim 1 wherein the three-dimensional catalyst is a metal supported on an inert oxide or supported on a mixed ionic and electronic conducting oxide.

13. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst are selected from catalysts that promote the partial oxidation of methane or higher hydrocarbons to CO and hydrogen.

14. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst are selected from catalysts that promote the partial oxidation of hydrocarbons to oxygenated species.

15. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst are selected from catalysts that promote the partial oxidation of hydrocarbons to epoxides.

16. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst are selected from catalysts that promote the oxidative dehydrogenation of alkanes.

17. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer and the three-dimensional catalyst are selected from catalysts that promote the oxidative coupling of methane or higher hydrocarbons.

18. The catalytic membrane reactor of claim 1 wherein the adherent catalyst layer protects the membrane from decomposition.

19. A catalytic reactor membrane having an oxidation surface and a reduction surface with an adherent catalyst layer on the oxidation surface wherein the membrane comprises a ceramic of the formula:

$$A_{2-x}A'_xB_{2-y}B'_yO_{5+z}$$

where A is an alkaline earth metal ion or mixture of alkaline earth metal ions; A' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of metals of the lanthanide series and yttrium; B is a metal ion or mixture of metal ions wherein the metal is selected from the group consisting of 3d transition metals, and the group 13 metals; B' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, the group 13 metals, the lanthanides and yttrium; x and y are,

independently of each other, numbers greater than or equal to zero and less than or equal to 2; and z is a number that renders the ceramic material charge neutral.

20. The catalytic reactor membrane of claim 19 wherein the adherent catalyst layer is a mixed ionic and electronic conducting ceramic of the formula:

$$X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X is Ca, Sr or Ba, or mixtures thereof Re is a rare earth or lanthanide metal, including yttrium, or mixtures thereof, Z is Al, Ga or In or mixtures thereof and Z' is Cr, Mn, Fe or Co or mixtures thereof, with a and b numbers such that $0 \leq a \leq 1$ and $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that renders the composition charge neutral.

21. The catalytic reactor membrane of claim 19 wherein the adherent catalyst layer is a mixed ionic and electronic conducting material of the formula:

$$M/X_aRe_{1-a}Z_bZ'_{1-b}O_c$$

where X is Ca, Sr or Ba, or mixtures thereof, Re is a rare earth or lanthanide metal, including yttrium, or mixtures thereof, Z is Al, Ga or In or mixtures thereof and Z' is Cr, Mn, Fe, Co, Cr, V. Mo, W or mixtures thereof, with a and b numbers such that $0 \leq a \leq 1$ and $0 \leq b \leq 1$ and c is a number, dependent upon the oxidation states of the other components, and the values of a and b, that renders the composition charge neutral and M is a metal selected from Ni, Pt, Pd, Rh, Ir, Ag or mixtures therof and wherein the weight percent of metal to mixed conducting material ranges from about 1wt% to about 50wt%.

22. The catalytic reactor membrane of claim 19 wherein the adherent catalyst layer prevents decomposition of the membrane.

23. A catalytic membrane reactor of claim 3 for the production of synthesis gas by oxidation of a methane-containing gas wherein the adherent catalyst layer is a ceramic exhibiting both ionic and electronic conduction and the three-dimensional catalyst comprises a first row transition metal ion in a weakly basic matrix.

24. The catalytic membrane reaction of claim 6 wherein the oxygen reduction catalyst is a metal selected from the group Pd, $La_aSr_{1-a}CoO_{3-x}$, where a is a number such that $0 \leq a \leq 1$ and x is a number such that the compound is charge neutral.

25. The catalytic membrane reactor of claim 23 wherein the oxygen reduction catalyst is Pd (5wt%) on $La_{0.8}Sr_{0.2}Co\ O_{3-x}$, the adherent catalyst layer is Ni (20wr%) on $La_{0.8}Sr_{0.2}Nm\ O_3$ and the three dimensional catalyst is Ni (5wr%) on alumina.

26. A method for oxidizing a reactant gas which comprises the steps of:

(a) providing a catalytic membrane reactor of claim 1;

(b) introducing a reactant gas into the oxidation zone of the reactor;

(c) introducing an oxygen-containing gas into the reduction zone of the reactor; and

(d) heating the oxygen ion-conducting, gas-impermeable membrane separating the oxidation zone and the reduction zone to effect reduction of the oxygen-containing gas and transport of oxygen ions to the oxidation zone and effect oxidation of the reactant gas.

27. A method for oxidizing a reactant gas and reducing an oxygen-containing gas which comprises the steps of:

(a) providing a gas-impermeable, oxygen ion-conducting membrane separating and forming an oxidation zone and a reduction zone;

(b) providing a three-dimensional catalyst in the oxidation zone separated from, but in contact with membrane surface;

(c) contacting the reactant gas with the membrane surface and the three-dimensional catalyst in the oxidation zone;

(d) contacting the oxygen-containing gas with the membrane surface in the reduction zone;

(e) heating the membrane to effect reduction of the oxygen-containing gas, generating oxygen ions at the surface of the membrane in the oxidation zone and effecting oxidation of the reactant gas at the membrane surface, at the three-dimensional catalyst or both.

28. The method of claim 27 wherein in step (a) the gas-impermeable membrane is provided with an adherent catalyst on its surface in contact with the oxidation zone.

29. The method of claim 28 wherein the reactant gas is methane, or a methane-containing gas which is oxidized to produce synthesis gas.

30. The method of claim 28 wherein the reactant gas is a higher hydrocarbon, mixture of higher hydrocarbons or a mixture of higher hydrocarbons with methane.

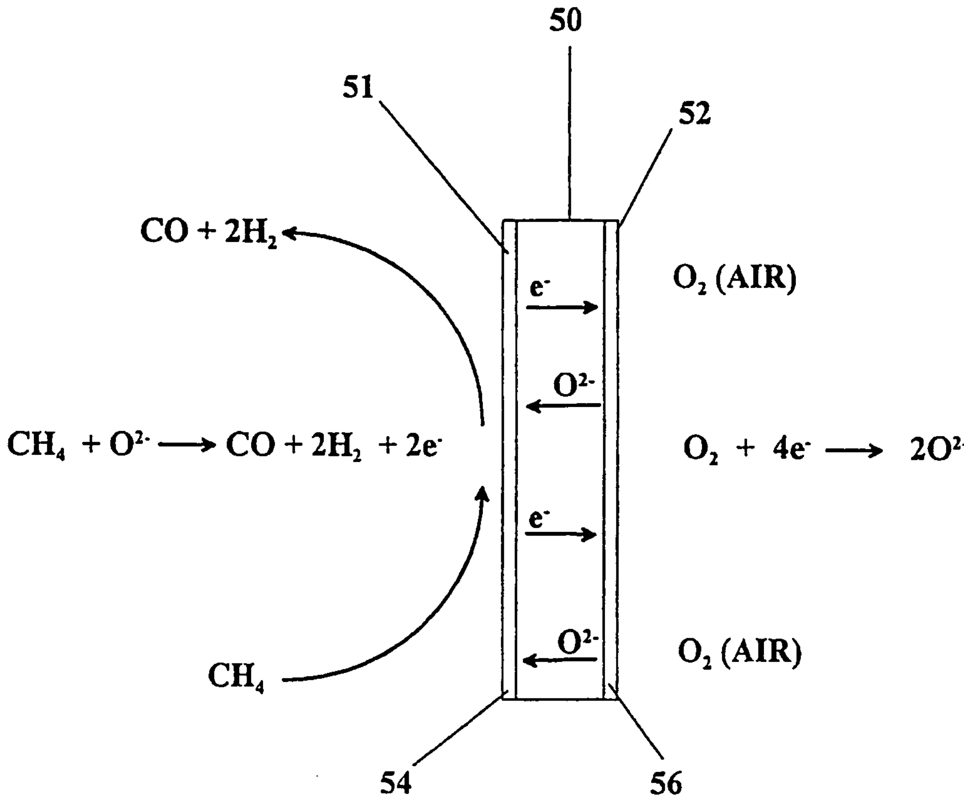
50
51
52
$CO + 2H_2$
e^-
O_2 (AIR)
O^{2-}
$CH_4 + O^{2-} \longrightarrow CO + 2H_2 + 2e^-$
$O_2 + 4e^- \longrightarrow 2O^{2-}$
e^-
O^{2-}
O_2 (AIR)
CH_4
54
56

FIGURE 1

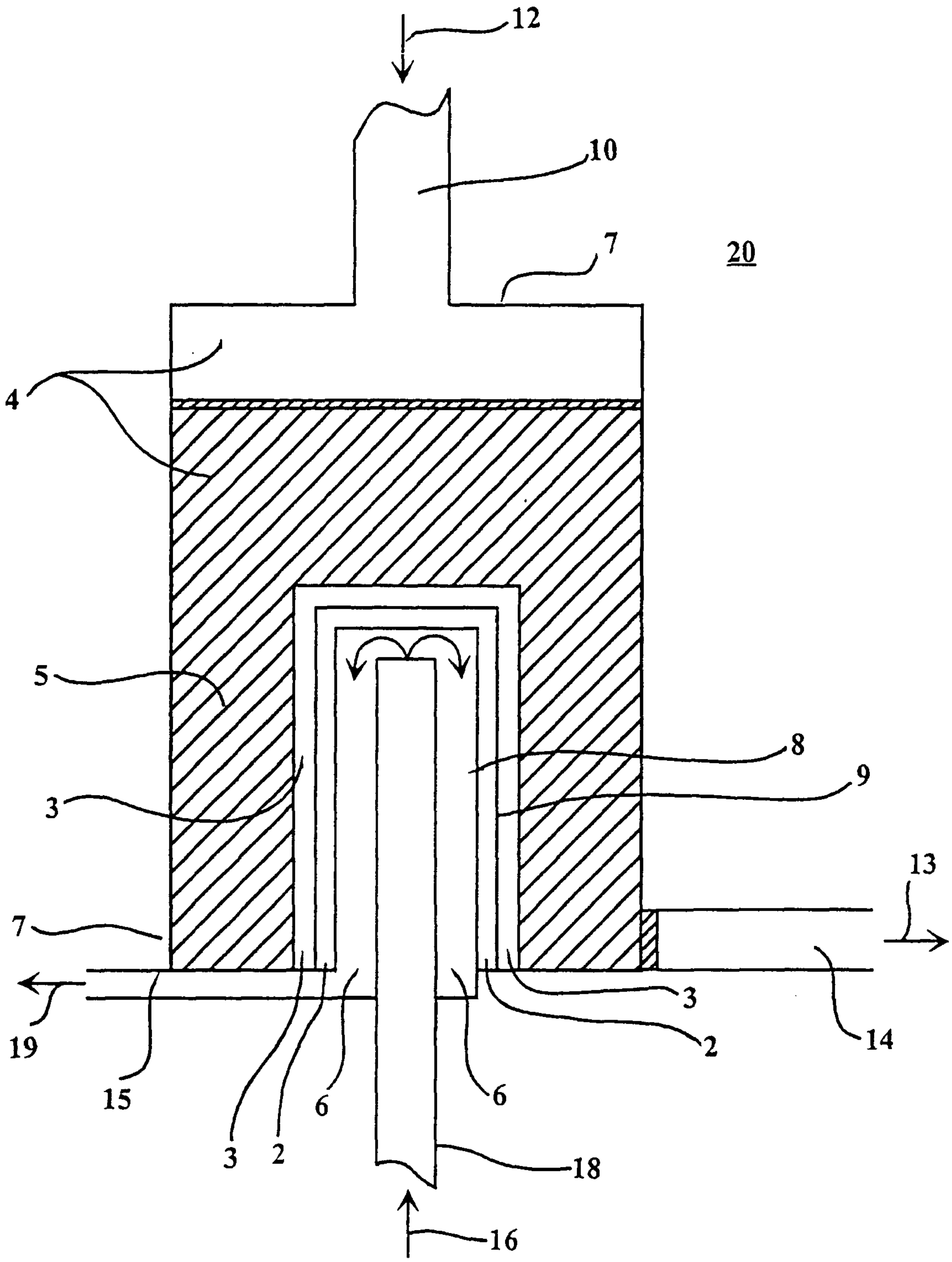

FIGURE 2

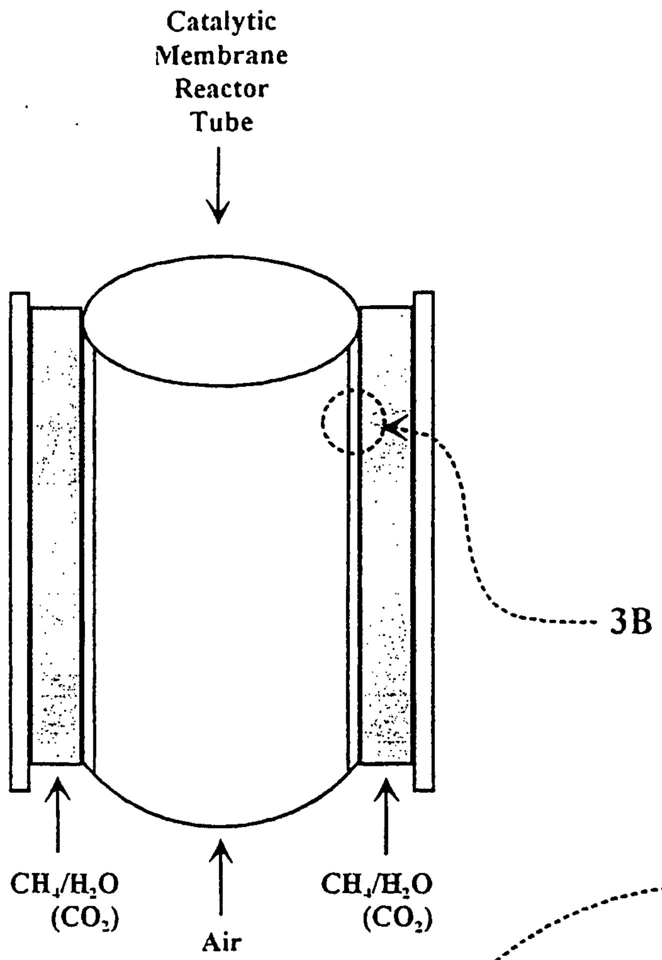

FIGURE 3A

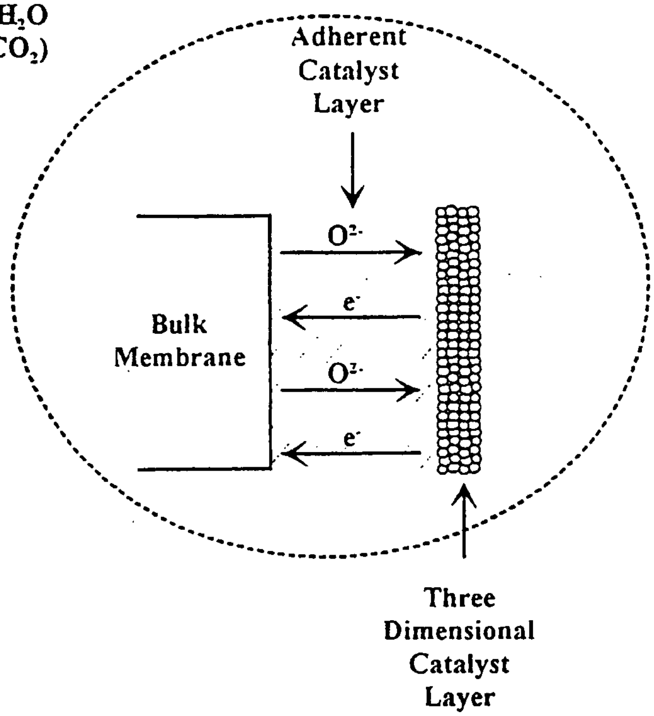

FIGURE 3B

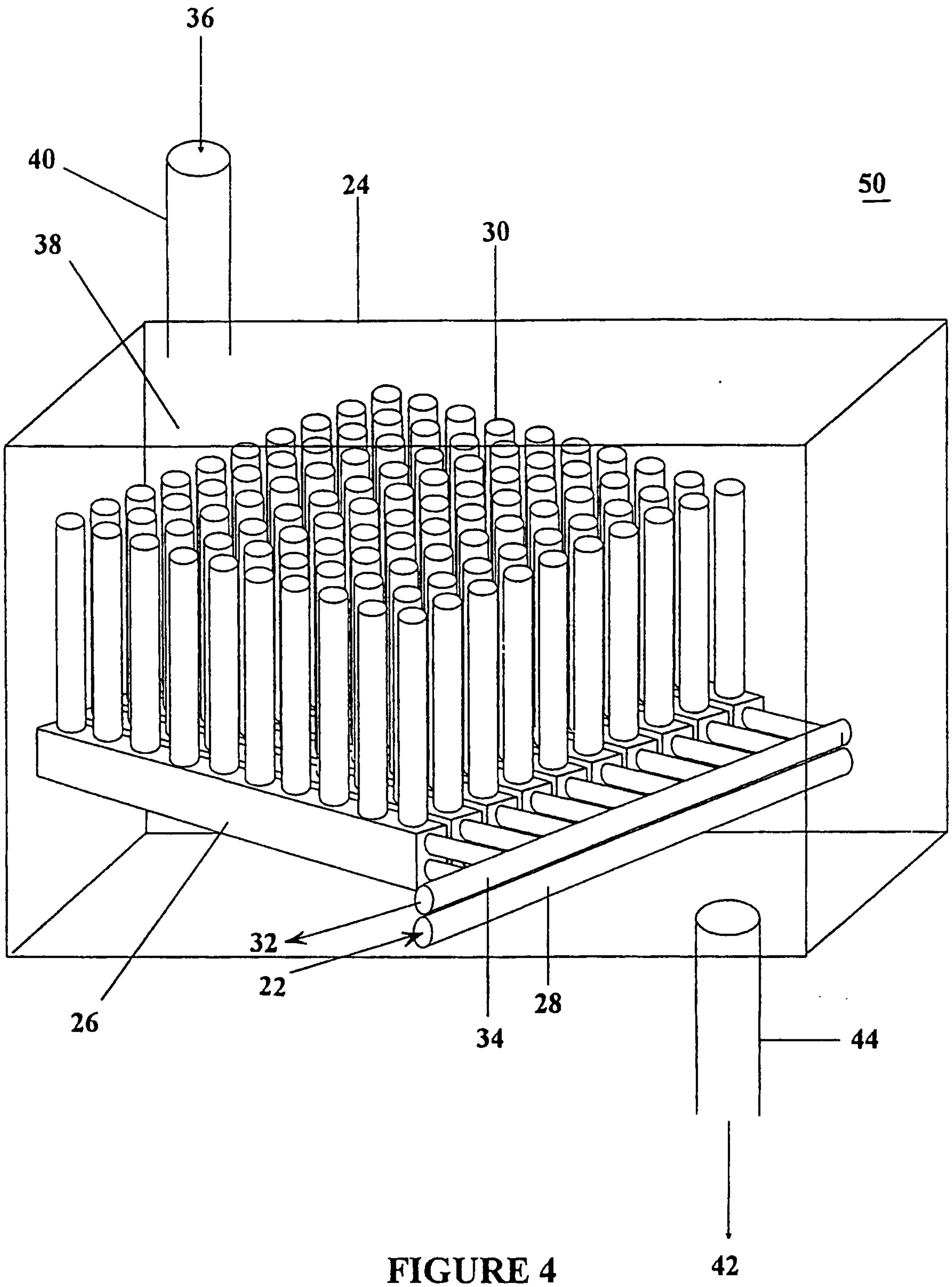

FIGURE 4

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/US 98/23051

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J19/24 B01J19/00 B01J23/00 B01J35/06 B01J12/00
B01D71/02 B01J8/02 C01B13/02 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J B01D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 97 41060 A (ELTRON RESEARCH, INC.) 6 November 1997 cited in the application see claims; figures	19
P,A		1-18, 20-30

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
24 February 1999	12/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stevnsborg, N

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	M. SCHWARTZ ET AL.: "The use of ceramic membrane reactors for the partial oxidation of methane to synthesis gas" PREP. PAP. - AM. CHEM. SOC., DIV. FUEL CEM., vol. 42, no. 2, 1997, pages 596-600, XP002094539 us see the whole document -& CHEMICAL ABSTRACTS, vol. 126, no. 18, 5 May 1997 Columbus, Ohio, US; abstract no. 240509, M. SCHWARTZ ET AL.: "The use of ceramic membrane reactors for the partial oxidation of methane to synthesis gas" XP002094550 see abstract ---	1-30
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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